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Recent advances in membrane distillation processes: Membrane development, configuration design and application exploring

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ABSTRACT

Membrane distillation (MD) is a separation process based on the vapor transport across the hydrophobic microporous membrane driven by the vapor pressure gradient across the membrane. This process can be used for various applications such as seawater desalination, wastewater treatment, separation of volatile compounds, concentration of non-volatile compounds and processing of dairy fluids. Comparing with other separation processes, the MD process possesses unique characteristics such as 100% (theoretical) rejection, mild operation conditions, insensitive to feed concentration and stable performance at high contaminant concentrations. Due to high oil prices in recent years, extensive research has been devoted to MD in the areas of membrane materials, module configurations, process applications and hybrid systems. This review aims to summarize the recent advances in MD and provide perspectives for its future R&D.

Contents

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1. Introduction

Membrane distillation (MD) is an emerging membrane technology based on the vapor pressure gradient across the porous hydrophobic membrane. Since only volatile vapor molecules can transport across the membranes, the feed liquid directly contacting the membrane must not be allowed to penetrate into the dry pores of the hydrophobic membranes [1–8]. As illustrated in Fig. 1.1, the hydrophobic nature of the MD membrane prevents the feed liquid from entering membrane pores due to the surface tension. Meanwhile, the volatile components in the hot feed vaporize at the liquid/vapor interface and diffuse across the dry membrane pores. The vapors are then collected or condensed by different methods.

Comparing with other membrane separation processes, MD offers a number of advantages: (1) 100% (theoretical) rejection of inorganic ions, macromolecules and other non-volatile compounds, (2) relatively low operating temperatures, (3) lower operating pressures than conventional pressure-driven membrane separation processes, (4) insensitive to feed concentration for seawater desalination, and (5) less requirements on membrane mechanical properties [1–10]. With these unique advantages, MD processes have demonstrated promising results in seawater desalination, wastewater treatment and many other applications [11–16].

The first MD patent was issued in 1963 [17]. Lawson et al. conducted an in-depth review on MD and its historical development [1]. Comprehensive reviews were then made by Alklaibi and Lior [18], Tomaszewska [19], Curcio and Drioli [15,16], El-Bourawi et al. [20]. The applications of MD process for desalination and water purification have been reviewed by Gryta [14], Camacho et al. [10] and other research teams [21,22]. Khayet has reviewed the theoretical modeling of MD process [23].

The commercialization of MD process has been constrained mainly by two factors; namely, 1) the lack of commercially available high performance membranes and 2) high energy consumption [24,25]. To expand and fully harvest the advantages of MD process, new MD applications and hybrid systems must also be explored. In this work, we aim to review the recent advances in MD technology in terms of membrane development, energy-saving configuration design, system hybridization and exploration of new applications.

Firstly, design of suitable MD membranes will be reviewed from the aspects of membrane materials and fabrication. As a microporous physical barrier, the desired MD membrane must have excellent anti-wetting properties, high flux and resistance towards high temperature, potential fouling and scaling [15,16,18,23].

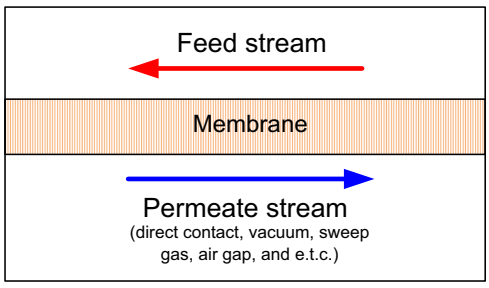


Fig. 1.1. Illustration of the MD process.

Membrane wetting happens during continuous MD operations. Better wetting resistance requires a membrane with higher hydrophobicity and uniformly distributed smaller pores [1]. With a coupled heat and mass transport mechanism, a high flux MD membrane should have low vapor transfer resistance and low thermal conductivity to prevent heat loss across the membrane [10–26]. In addition, MD membranes should have good thermal stability and chemical stability (e.g. acid and base) in order to handle the elevated operating temperatures and chemical cleaning [19].

The second portion of this review focuses on the improvement of energy efficiency in the design of various configurations. As a distillation-based process, the MD process involves in the latent heat of water vaporization and condensation. Without a heat recovery design, a minimum energy consumption of around 628 kWh is needed for MD to produce one ton of clean water, while the state-of-art reverse osmosis (RO) technology only needs 2–3 kWh/m^3 [23,27]. Hence, extensive efforts are needed to design MD configurations with reduced energy consumption.

The last portion of this review emphasizes on the exploration of new MD applications. Examples include seawater desalination, treatment of wastewater containing specific contaminants, concentration of non-volatile compounds and separation of volatile compounds from its aqueous solutions.

2. Membrane development

One of major difficulties in MD processes is the lack of commercially available MD membranes with high performance, sufficient wetting resistance and minimized fouling/scaling tendency. Without a suitable membrane, it is hard to materialize MD as a viable separation technology. Among the materials investigated or utilized for MD membranes, hydrophobic polymers are preferred due to their characteristics of easy fabrication, modification, and scale-up as well as low costs [15,16]. Different fabrication processes such as nonsolvent induced phase separation (NIPS) [28–30], thermally-induced phase separation (TIPS) [31], melt extrusion stretching [32], sintering [33], electro-spinning [34] and other technologies have been employed to fabricate MD membranes depending on polymer properties and applications. In recent years, ceramic, carbon nanotubes (CNTs) and metals have also been explored as membrane materials for some MD studies [35–38].

2.1. Membrane materials and fabrication

Since hydrophobicity is the essential requirement for MD membranes in most applications, the membranes must be made from intrinsic or modified hydrophobic polymers with low surface energy. Materials such as silicone coated glass fibers and nylon were investigated in the early stage of MD development but showed unsatisfactory wetting resistance [39]. Table 2.1 shows the characteristic properties of commercially available low surface energy polymers commonly used for MD membranes. So far, the most popular polymers used in MD membranes are still polytetrafluoroethylene (PTFE), polypropylene (PP) and polyvinylidene fluoride (PVDF) [10,23,40,41].

PTFE has the lowest surface energy of around $9-20\times10^{-3}$ N/m [45]. It is a highly crystalline polymer with excellent thermal stability and chemical resistance. Since PTFE is a non-polar polymer,

it is difficult to fabricate PTFE membranes by common NIPS and TIPS processes. The hydrophobic PTFE membranes used for MD applications are normally produced using sintering method or melt-extrusion method [46–48]. PTFE membranes are most often used in the commercial and pilot MD systems because of their good wetting resistance, satisfactory water flux and excellent stability in various operation conditions [49–51].

The sintering process begins with a mixture of very fine PTFE powders and volatile lubricating agents (e.g. hydrocarbon) [46,48,52]. The formed paste is then extruded into a sheet or hollow fiber forms which is then heated and expanded in order to produce a microporous membrane. The membrane needs to be stabilized in an amorphous locking step by thermal annealing. As an example of the sintering process, Gore fabricated a highly-porous PTFE membrane using a paste with PTFE powder and volatile lubricant Isopar™ isoparaffinic fluids (ExxonMobil Chemical) [53]. After removing the volatile lubricant by drying, the paste was bi-axially stretched for five times at 225 °C to generate the highly-porous structure. The final amorphous locking process was carried by annealing the membrane at 370 °C for 5 mins.

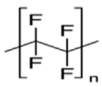
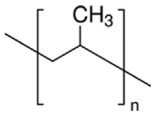
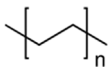
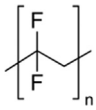
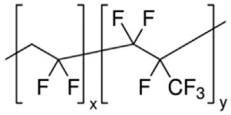
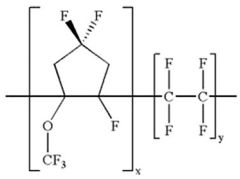
The polymer melt extrusion method followed by stretching is also used for PTFE membrane fabrication [47,48]. PTFE films are obtained by extruding PTFE melt coupling with a rapid draw down during the stretching. After the annealing and cooling processes, a mechanical stress is applied to the direction of drawing so that a relatively uniform porous structure is formed with a pore size distribution in the range of 0.2–20 μm [54].

PP also has a highly crystalline structure but higher surface energy (30.0×10^{-3} N/m) than PTFE [10]. Porous PP membranes such as Celgard® have been fabricated by the melt-extrusion-stretching method by taking the unique hard elastic properties of PP [55–59]. Besides, PP membranes are also fabricated by the TIPS process [60,61]. In this method, a homogeneous solution is firstly formed by dissolving PP in diluents at a temperature above T_m. Inert gas such as nitrogen is often introduced to avoid oxidation. Once the membranes are fabricated by casting or spinning, solid-liquid separation and liquid-liquid separation as well as diluent extraction take place. Eventually, a porous membrane is formed. In some cases, the resultant membranes are further stretched from single/dual directions to re-align the crystal structure and balance the mechanical properties. Fig. 2.1 (A) and (B) show PP membranes with elliptical pores fabricated from the melt-extrusion-stretching method and circular pores fabricated from mono-axially stretching, respectively [56]. Recently, circular pores were also obtained by a bi-axially stretching after the melt-extrusion process [62]. As compared with other MD membranes, PP membranes are relatively advantageous in material and manufacturing costs. However, the membrane performance is generally lower due to the symmetric structure and the moderate thermal stability at elevated temperatures. These may limit PP potential for MD applications [32].

PVDF is a semi-crystalline polymer with a surface energy of 30.3×10^{-3} N/m. Unlike PTFE and PP, it can be easily dissolved in common solvents such as n-Methyl-2-Pyrrolidone (NMP), dimethylacetamide (DMAC) and dimethylformamide (DMF). Meanwhile, it has a relatively low melting temperature of 170 °C. Therefore, PVDF membranes can be fabricated either by NIPS, TIPS or a combination of TIPS and NIPS process [65–71]. Fig. 2.2 shows the SEM images of micro-porous PVDF membranes fabricated by the two methods. PVDF membranes fabricated via TIPS tend to have a relatively uniform porous structure without macrovoids, while most of PVDF membranes fabricated via NIPS possess an asymmetric structure consisting of a dense surface and many macrovoids in the cross-section [41,69,72–74].

Utilizing the aforementioned polymers, membranes with flat sheet and hollow fiber configurations have been fabricated by both membrane manufacturers and researchers. For example, flat sheet PTFE membranes with polyester (PET) or PP supports have been produced by companies such as PALL, Gore, Membrane Solutions and GE [10]. Hollow fiber PTFE membranes have been produced by Toyobo and

Table 2.1
Characteristic properties of commercial polymer materials commonly used for MD membranes [10,23,40–44].

Polymer materials	Chemical structure	Surface energy ($\times 10^{-3}$ N m^{-1})	Thermal conductivity (W m^{-1} K^{-1})	Thermal stability	Chemical stability	Fabrication methods
PTFE		9–20	0.25	Good	Good	Sintering Melt-extrusion
PP		30	0.17	Moderate	Good	Melt-extrusion TIPS
PE		28-33	0.40	Poor	Good	Melt-extrusion TIPS
PVDF		30.3	0.19	Moderate	Good	NIPS TIPS Electro-spinning
PVDF-HFP		–	–	Good	Good	NIPS Electro-spinning
Hyflon®		–	0.2	Good	Good	NIPS

several research groups [75]. Similarly, flat sheet and hollow fiber PP membranes are commercially available as Celgard® (Pollypore) and ACCUREL® (Membrana) [76,77]. Gryta and his co-workers have thoroughly evaluated the application of PP hollow fiber membranes for MD applications [78,79].

In addition to homo-polymers of PP, PVDF and PTFE, MD membranes can be made from their copolymers with enhanced hydrophobicity and durability. Hyflon® AD (Solvay Plastics), the copolymer of tetrafluoroethylene (TFE) and 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole (TTD), has been used by Gugliuzza and Drioli and Arcella et al. to prepare asymmetric membranes with a contact angle large than 120° [80,81]. Garcio-Payo et al. fabricated a series of hollow fiber membranes using poly (vinyldiene fluoride-co- hexafluoropropylene) (PVDF-HFP) [29,82]. Nunes and her co-workers fabricated MD membranes from aromatic fluorinated polyoxadiazoles and polytriazoles by both phase inversion and electro-spinning methods [83]. The resultant membranes exhibited high porosity and super-hydrophobicity with an apparent contact angle up to 162° [84].

Besides using intrinsic hydrophobic polymers, MD membranes can also be made from hydrophilic polymer materials that have undergone hydrophobic modifications. Plasma polymerization provides a powerful technology to modify the membrane surface. Fluorine-containing monomers can be activated with plasma sources to form a branched polymer and adhere to membrane surface [85]. For example, hydrophilic polyethersufone (PES) ultrafiltration (UF) hollow fiber membranes can be plasma modified by CF_4 monomer and converted to hydrophobic membranes for MD [86]. The plasma modified membranes displayed a contact angle of around 120°. During the 54 h DCMD test, the modified PES membrane exhibited a stable water flux of 66.7 l m^{-2} h^{-1} (LMH) and a salt rejection as high as 99.97% at 73.8 °C. Similarly, Kong et al. modified a cellulose nitrate (CN) membrane via plasma polymerization of octafluorocyclobutane [87]. In another work, surface modified poly(phthalazinone ether sulfone ketone) (PPESK) membranes were used for vacuum membrane distillation (VMD) [88]. After surface-coating modifications by silicone rubber and sol-gel polytrifluoropropylsiloxane, the PPESK hollow fiber membrane exhibited a more hydrophobic surface with a contact angle of 110° and a higher liquid entry pressure (LEP) of 0.12 Mpa. The permeation flux of silicone rubber composite membranes was affected by the formulation of coating solutions and the membrane with the optimal formulation exhibited a high salt rejection of 99%.

Aside from polymeric materials, metal, glass, CNTs and inorganic based materials were also evaluated for MD applications [38,89–91]. Similar with the hydrophilic polymers used in MD processes, ceramic membranes (i.e., zirconia, alumina and titanium) need to be modified for improved hydrophobicity [35–38]. For example, surface modified zirconia membrane with a pore diameter of 50 nm exhibited a high rejection and a reliable air gap membrane distillation (AGMD) flux of around 4.7 LMH and close to 100% salt rejection (converted from the original unit) at a feed temperature of 95 °C. Recent works also investigated the assembly of CNTs into paper-like structures called Bucky-Papers (BP) as self-supporting membranes, where the CNTs were held together solely by Van der Waals forces [92]. The ultra-thin BP membranes with a

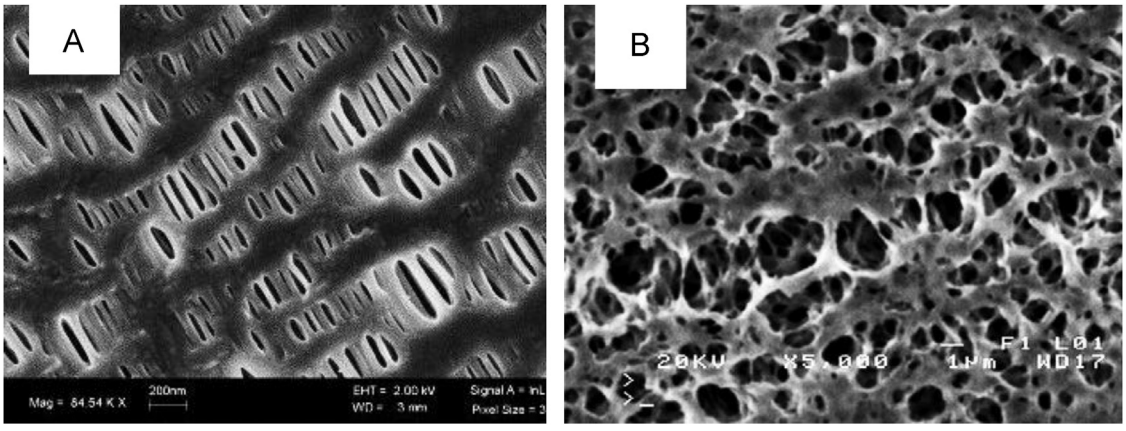


Fig. 2.1. SEM images of micro-porous PP membranes fabricated from (A) a melt-extrusion-mono-axially-stretching, (B) TIPS methods [63,64].

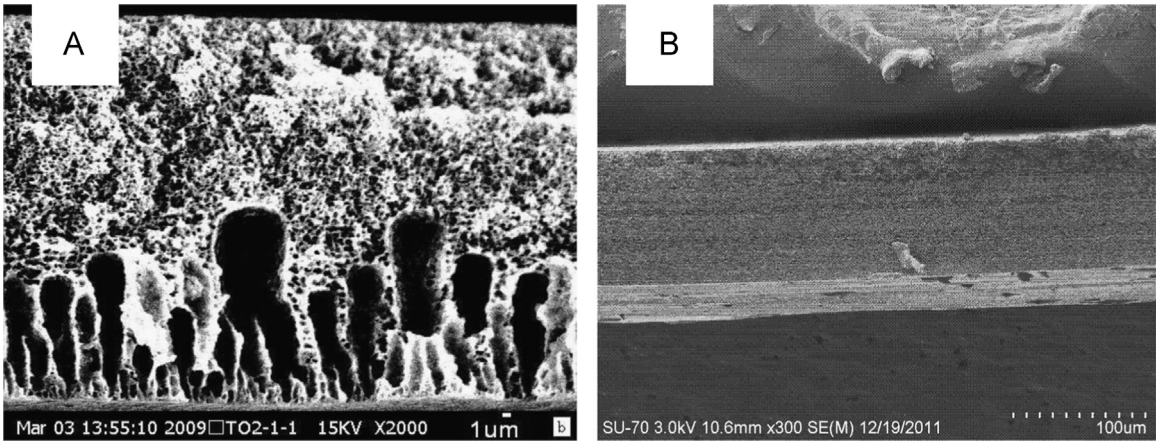


Fig. 2.2. SEM Image of a PVDF micro-porous membrane fabricated from (A) NIPS and (B) TIPS methods [65,72].

narrow pore size were processed by vacuum filtration of CNTs dispersed in 99.8% pure 2-propanol. The self-supporting CNT BP membrane showed a DCMD flux of 12 LMH with 99% salt rejection at a water vapor partial pressure difference of 22.7 kPa. However, aging and delamination were observed, improvements such as surface grafting and coating have to be carried out to improve membrane durability [93].

Hydrophobic materials have been used in the MD process for seawater desalination and alcohol/water separation due to its large surface energy gaps with water [94–96]. However, in the case of oil-like liquids, either hydrophilic or super-hydrophobic materials are preferred to produce an oleophobic surface [97]. Qu et al. compared the VMD performance of hydrophobic PVDF and hydrophilic polyacrylonitrile (PAN) membranes for the recovery of petroleum ether from the solanesol extracting solution [97]. The hydrophilic PAN membrane showed a good VMD flux (> 15 LMH) and solute rejection (> 98%), while the hydrophobic PVDF membrane was easily wetted and lost its selectivity. Fig. 2.3 illustrates the transport mechanisms of a feed mixture of solanesol and organic solvents across hydrophilic and hydrophobic membranes in MD processes. A hydrophobic membrane will be easily wetted due to the high affinity between the organic solution and the hydrophobic membrane material. Yet in a hydrophilic membrane, the volatile solvent evaporates from the liquid-vapor interface on the feed side and then diffuses across the membrane pores.

2.2. *Polymer blend and additives & modification*

In most membrane manufacturing processes such as NIPS, TIPS or melt-extrusion, the incorporation of additives in dope formulation is an effective and widely used method to design a MD membrane with desirable morphology, permeation performance, hydrophobicity or anti-fouling properties. The choice of pore forming agents such as small molecule nonsolvents, inorganic salts or macromolecules as well as their combinations plays an important role in determining membrane formation and separation performance.

Water, alcohols, ethylene glycerol (EG) and poly-ethylene-glycerol (PEG) are the examples of small-molecule pore forming agents that have been widely used in membrane fabrication, especially for NIPS, to enhance flux and control the pore sizes [30,98]. As non-solvents in the PVDF-solvent binary system, the addition of liquids with lower polymer solubility may increase dope viscosity as well as bring the solution closer to the gelation point. As a result, the resultant membranes may have a more porous structure at membrane cross-section and surfaces. Inorganic salts like LiCl are also employed during membrane preparation [30,99]. The complex formed between Li^+ and electron donating groups of solvents could increase dope viscosity, affect dope precipitation rate, and enhance the permeation properties by producing larger pores and higher porosity. Tomaszewska pioneered the works of utilizing LiCl to prepare PVDF MD membranes [28]. The addition of LiCl into the casting solution drastically altered the membrane structure to an asymmetric porous structure with large macrovoids. The membrane hydrophobicity was also increased after drying. Similarly, lithium perchlorate ($LiClO_4$) was used as a pore forming agent in the fabrication of PVDF hollow fiber membranes [100]. With an addition of 3 wt% $LiClO_4$, the pore size of the membrane increases from ~10 nm to ~50 nm and no obvious change of pore size distribution was observed.

Besides small molecules and inorganic salts, macromolecules are also utilized as pore forming additives. Polyvinylpyrrolidone (PVP) with different molecular weights are used to (1) prepare membranes with desirable pore sizes and porosity, (2) form hydrophilic membranes and (3) reduce bio-fouling [101,102]. Simone et al. fabricated microporous hydrophobic PVDF hollow fibers by utilizing water and PVP as the pore forming additives [103]. Interestingly, PVP promotes the formation of macorvoids when the PVP concentration is low. In contrast, it helps form a sponge-like structure with high porosity when its concentration is high. The obtained fibers exhibited a high porosity (up to 80%) and optimized pore size. In literatures, there are still concerns about the usage of PVP in MD membranes due to its hydrophilicity. However, the membranes in their work showed stable long-term performance up to 2 months for VMD tests even though the contact angle was not reported.

Mixed matrix membranes are known to improve physicochemical properties of various membranes [104–110]. By incorporating micro- or nano- size particles, one can change solution rheology, alter phase inversion and control membrane morphology. Meanwhile, the mixed matrix membranes could gain specific benefits from particles with various hydrophilicity, hydrophobicity or anti-fouling properties. Wang et al. fabricated nano-porous mixed matrix hollow fiber membranes by using hydrophobic modified nano-clay particles [107]. The fabricated membranes had finger-like macrovoids and exhibited a high flux of 72 LMH and close to 100% salt rejection at a feed temperature of 80 °C. Similarly, Teoh, Chung and their coworkers incorporated PTFE micro-particles into the PVDF polymer solution [111–113]. The resultant membranes showed a high contact angle of about 130°. In another work, Edwie et al. blended fluorinated silica particles (FSi) with a PVDF solution [114]. The fabricated membranes showed highly hydrophobic characteristics with a contact angle of 147.5° and performed well in 5-day continuous DCMD experiments.

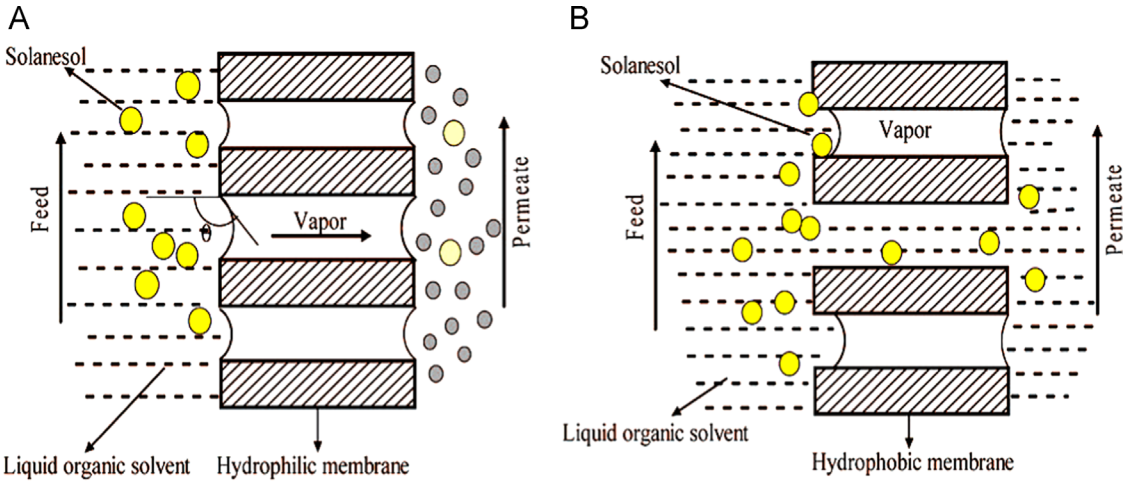


Fig. 2.3. Schematic presentation of MD process with (a) hydrophilic membrane and (b) hydrophobic membrane [97].

In previous sections, methods as plasma or chemical polymerization to modify a hydrophilic membrane have been reviewed. Similarly, Chen and her co-workers utilized sol-gel prepared TiO_2 nanoparticles to modify the MD membranes [115]. The water contact angle increased from 125° to 166°. The membrane was able to maintain its super-hydrophobic property after fouling tests using model seawater and humic acid solutions. CNTs were also employed to modify the membrane surface inside pores [116]. The incorporation of CNTs led to a significant increase in MD performance (i.e., 1.85 times increase in flux). The authors believed that the additional diffusion path and the enhanced pore hydrophobicity were responsible for the improvements. Interestingly, the membrane showed high salt rejection (99%) at lower feed salinity (10 mg/L) but low rejection (15%) at higher salinity (34000 mg/L).

2.3. Membrane geometry and micro-structure

The structure and chemistry of MD membranes are critical in achieving high and stable performance. Basically, the membranes must be designed with the maximal vapor transportation but minimal wetting or fouling [117]. As compared with other UF and MF membranes, the macro-geometry and micro-structure of MD membranes play more important roles in determining membrane performance.

It has been pointed out that membranes with large pores and high porosity are preferred for vapor transport, while wetting by contacting liquids or contaminants should not occur [118]. Unlike other membrane separation processes, permeation flux for a MD membrane can be affected two possible mechanisms; namely, vapor transfer resistance and temperature polarization effect [7]. Via the first mechanism, the mass transfer resistance can be minimized by fabricating membranes with large pore sizes and porosity, open-cell pore structure, thin functional layer and small tortuosity. Through the second mechanism, the flux decline due to temperature polarization can be mitigated by reducing the thermal conductivity across the membrane. Since the thermal conductivity of air inside membrane pores is much lower than that of the polymer matrix, one can lower thermal conductivity by increasing membrane porosity [107].

During the continuous MD operation, there is a risk of pore wetting by vapor condensation and liquid penetration. At the worst situation, entirely wetted pores would result in the loss of membrane selectivity when the feed and permeate solutions at both streams are in direct contact [19]. Therefore, wetting of membrane pores should always be avoided. To improve the wetting resistance and LEP, a membrane of high hydrophobicity, small pore size and high tortuosity is highly desired [108,114,119].

Traditionally, there are two common types of membrane macro-geometries: (1) Hollow fiber membranes and (2) Flat sheet membranes. Comparing to flat sheet membranes with plate & frame and spiral-wound configurations, hollow fiber membranes have larger specific surface areas [120]. A typical plate & frame or spiral wound module has a packing density of 200–800 m^2/m^3, while that of a hollow fiber module could range from 500–9000 m^2/m^3 [121]. However, the main drawbacks of current MD hollow fibers are low flux, weak mechanical properties and higher risk of scaling and clogging [117–129].

In order to maximize vapor diffusion, permeation flux and thermal efficiency, the desired MD membrane is preferably to have a high porosity and a relative large pore size in the range of 0.1–0.3 μm to reduce the mass transfer resistance and minimize the temperature polarization [108,119,123,124]. However, the large pore size and high porosity in both bulk and surfaces also cause membranes suffering from weak mechanical properties in both axial and radial directions. To overcome it, Wang et al. and Teoh et al. pioneered multi-bore hollow fiber (MBF) and rectangular membranes for various MD applications [30,125–127]. In their works, the detailed formation mechanisms, spinneret design and effects of spinning parameters were explored. Fig. 2.4 shows the microscopic images of the round and rectangular MBF membranes. The MBF membranes fabricated from the optimal spinning conditions not only demonstrated high permeation fluxes (67 LMH at 90 °C feed temperature), but also exhibited superior stability and robustness in long term operation tests [126]. During the 300 h DCMD operation, the MBF membranes maintained its permeation flux and 99.997% salt rejection.

The development of dual-layer hollow fiber membranes is another great innovation in membrane fabrication [128–130]. Emerging applications of dual-layer hollow fiber membranes include gas separation, forward osmosis (FO), biofuel pervaporation and many other applications [131–135]. During spinning, two polymer solutions with different compositions are co-extruded from the two channels of the tri-orifice spinneret [136]. In the field of MD membrane fabrication, the dual-layer hollow fiber technology has been used to produce (1) morphologically designed membranes and (2) hydrophilic/hydrophobic dual-layer hollow fiber membranes [7,108,137].

Due to the unique heat and mass transfer mechanisms, the permeation flux and long-term stability of a MD membrane are highly dependent on its micro-structure. Wang et al. analyzed the key morphological characteristics for these two parameters and proposed a dual-layer hollow fiber consisting of a fully finger-like macrovoid inner-layer and a sponge-like outer-layer [7]. The outer layer with a sponge-like structure could maintain the wetting resistance, while the finger-like macrovoids could minimize the tortuosity and mass transfer resistance. In addition to high energy efficiency of 94%, a superior flux of 98.6 LMH was obtained during the DCMD desalination experiments with a feed inlet temperature of 80 °C.

The concept of hydrophilic-hydrophobic dual-layer membranes was initially introduced in the early 90's [138]. Illustrated in Fig. 2.5, the hydrophilic layer can be easily wetted by the permeated side water. This greatly reduces the functional layer thickness and transport distance of water vapors in MD processes. Khayet, Matsuura and their co-workers have worked on surface modified macromolecules (SMM), where the hydrophobic and hydrophilic segments of the SMM moved to top and bottom parts of the flat sheet membranes during the phase inversion processes [138–140]. Chung and his co-workers fabricated the hydrophilic-hydrophobic dual-layer hollow fiber membranes [108,109,114]. They used a mixture of PVDF/hydrophobic particles for the hydrophobic layer, while a blend of PVDF, PAN and hydrophilic clay as well as CNT for the hydrophilic layer. The use of PVDF in both layers was to improve molecular inter-diffusion and to avoid delamination between the dual-layer [108,137]. The best hollow fiber membrane they have made exhibited a water flux of 83.4 LMH at an 80 °C feed temperature.

The triple-orifice spinneret used in the dual-layer spinning can be also used to tailor the micro-structure of single-layer hollow fiber membranes. For example, by manipulating the shrinkage rates of these two layers during phase inversion, one can obtain single-layer macrovoid-free and highly permeable PVDF hollow fiber membranes for MD [137]. The right choices of dope and coagulant chemistry were the keys to induce de-lamination between these two layers. In another example, a single-layer MD fiber with high surface porosity was fabricated by applying the triple-orifice spinneret with a two-phase flow consisting of a solvent and a dope solution in the air-gap region during spinning [117]. In this approach, the dope solution and the solvent were co-discharged from the middle and outer channels of a triple orifice spinneret, respectively. It was observed that the outer solvent induced delay demixing that greatly enhanced the outer surface porosity and eliminated the macrovoid formation in the cross-section of the PVDF hollow fibers. The resultant fibers have two to

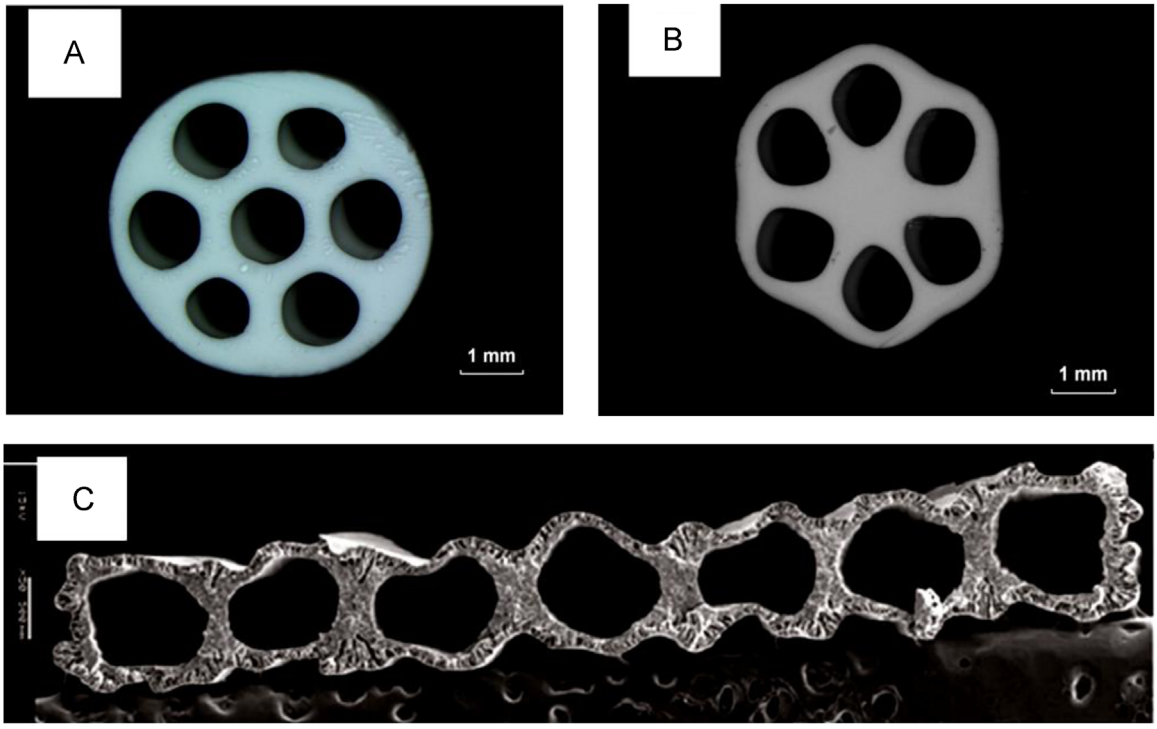


Fig. 2.4. SEM images of MBF PVDF membrane: (A) round-shape 7-bore (B) round-shape 6-bore and (C) rectangular 7-bore membranes [125–127].

three times higher fluxes than those obtained from the standard dry-jet wet-spun fibers.

Electro-spinning utilizes an electrical charge to draw extra fine fibers with a sub-micron diameter from a liquid form. Both polymer solution and polymer melt with a liquid form can be used for the electro-spinning process. Owing to the characteristics of the electro-spinning process, the membranes assembled from the electro-spun nanofibers have a non-woven like structure. This structure provides very high porosity and inner-connected pores [34,83,141,142]. Fig. 2.6 A) shows the mechanism and typical set-up of the electro-spinning process where nano- or micro-meter diameter polymer fibers can be evenly distributed on a support under high voltage. Shown in Fig. 2.6 B), the morphology of PVDF electro-spun membranes is very suitable for a MD application. Prince et al. fabricated PVDF-hydrophobic clay nano-composite membranes using the electro-spinning process. The addition of clay nano-particles in the electro-spun fibers increased the contact angle of MD membrane to 154.20° [34]. In other works, Liao et al. proposed heat-press post-treatment and super-hydrophobic modifications to improve the mechanical integrity and wetting resistance of electro-spun membranes [141,143]. Fig. 2.6 C) shows the micro-structure of modified electro-spun membranes with super-hydrophobic properties and multi-level roughness. Besides hydrophobic PVDF or PVDF-HFP materials, other polymers such as aromatic fluorinated polyoxadiazoles and polytriazoles, polystyrene (PS) and polyimide with rough surfaces were also evaluated for MD applications [44,83,144,145]. Tijing et al. conducted a comprehensive review on recent development of electro-spun membranes for MD applications [146].

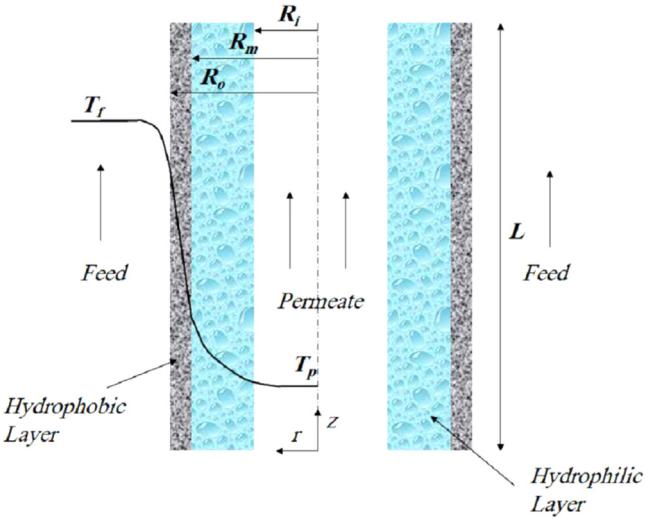


Fig. 2.5. The schematic illustration of a hydrophilic/hydrophobic dual-layer hollow fiber fabricated for DCMD [108].

3. MD configurations

Unlike pressure-driven membrane processes where permeate can be directly collected at the lower pressure side, the permeated vapor needs to be condensed via different methods. Depending on the methods to induce vapor pressure gradient across the membrane and to collect the transported vapors from the permeate side, MD processes can be classified into four basic configurations. The MD configuration plays an important role in determining the separation performance and operation cost. Some new configurations with improved energy efficiency, better permeation flux or smaller foot print have been proposed by many research teams [96,147,148]. In this chapter, we will review both basic and newly developed MD configurations.

3.1. Basic MD configurations

Fig. 3.1 illustrates the mechanisms of these four basic configurations [1].

(a) Direct contact membrane distillation (DCMD): An aqueous solution with a lower temperature is in direct contact with the

permeate side of the membrane. The temperature difference across the membrane induces the vapor pressure difference. Consequently, volatile molecules evaporate at the hot liquid/vapor interface, transport across the membrane pores in vapor phase and condense in the cold liquid/vapor interface at the permeate side. As the most simplified configuration, DCMD is widely studied in literature and laboratories for desalination and concentration of aqueous solutions [1–4,11,107–109,126,137,145,149–151]. As membrane is the only barrier to separate the hot feed and cold permeate solutions, DCMD has the highest conductive heat loss among four basic configurations.

(b) Air gap membrane distillation (AGMD): A thin air gap is designed between the membrane and a condensation surface (typically a thin dense polymer or metal film). The evaporated volatile molecules pass through both the membranes and the air gap and then condense on the cold surface [152,153]. As the air gap provides a significant vapor transport resistance, the flux of a typical AGMD is lower than DCMD or VMD configurations [154]. Utilizing the integrated cooling plate in the AGMD configuration, extensive works have been carried on the multi-effect or multi-stage membrane modules with improved thermal efficiency [155,156].

(c) Sweep gas membrane distillation (SGMD): A cold inert or sweep gas sweeps through the permeate channel and collects vapor molecules from the membrane surface. In most cases, the vapors are condensed outside the membrane module by an external condenser [157]. This could result in an additional equipment cost.

(d) Vacuum membrane distillation (VMD): Vacuum is applied at the permeate side of the membrane module. To provide the driving force, the applied vacuum must be lower than the saturation pressure of volatile molecules in the feed solution. Condensation may or may not occur outside of the membrane module [158–160]. SGMD and VMD are often used to remove VOCs from aqueous solutions [157,161–165].

3.2. New MD configurations

Comparing with RO, nanofiltration (NF) or MSF, MD can be operated at ambient pressure and lower temperature. However, the low thermal efficiency has limited the commercialization of MD process [166]. For example, the specific energy consumption of traditional MD configurations without heat recovery design can be easily higher than 1256 kwh/m^3 (estimated from gain output ratio) [15,166,167]. Hence, extensive works have been carried out to develop new MD configurations and membrane modules with higher thermal efficiency [49,96,147,168,169]. Some of these new configurations are introduced in this section.

3.2.1. Multi-stage and multi-effect membrane distillation (MEMD)

Fig. 3.2 illustrates the AGMD module consisting of internal heat recovery based on the concepts of multi-stage and multi-effect distillation for seawater desalination. The cold feed solution was placed beneath the condensation surface as a coolant to condense the permeated vapors as well as to gain heat. The pre-heated feed solution is further heated before it enters the feed channel.

The AGMD Memstil® MD module with heat recovery was developed in the late 1990 s by Netherlands Organization for Applied Scientific Research (TNO) and later licensed to Aquastil and Keppel Seghers for commercialization [147,148]. The module was designed with a spiral wound configuration. A heating source of 50–100 °C is supplied to the system. A micro-porous PTFE membrane was used in the module. The Memstill® module was designed for seawater and brackish water desalination [147]. Pilot desalination plants have been tested in Singapore, Netherland and other countries to address the technical issues [170]. After the pilot trials, Memstill® claimed to have a very low specific energy consumption of 56 to 100 kWh/m^3 [147,168]. Besides AGMD modules, DCMD modules with heat recovery were also developed based on the same technology [10]. Aquastill also announced the development of 24 m^2 module with counter-current flows [171].

The Sweden company, Scarab Development AB, developed the heat recovery AGMD module with a plate and frame design [172]. A microporous PTFE membrane from Gore-tex has been used in this module [173]. The energy consumption of this module was reported as 810 kWh/m^3 [154].

The Fraunhofer Institute for Solar Energy Systems (ISE) developed a full-scale multi-effect spiral-wound MD module with a membrane area of 5 or 14 m^2 and named it as permeate gap membrane distillation (PGMD) [96]. A typical PGMD module consists of a feed channel, hydrophobic membrane, permeate channel, condensation surface and condensate. The system enables feed pre-heating and permeate condensation within the membrane module. Fig. 3.3 shows the schematic and photos of spiral wound PGMD module [96]. With

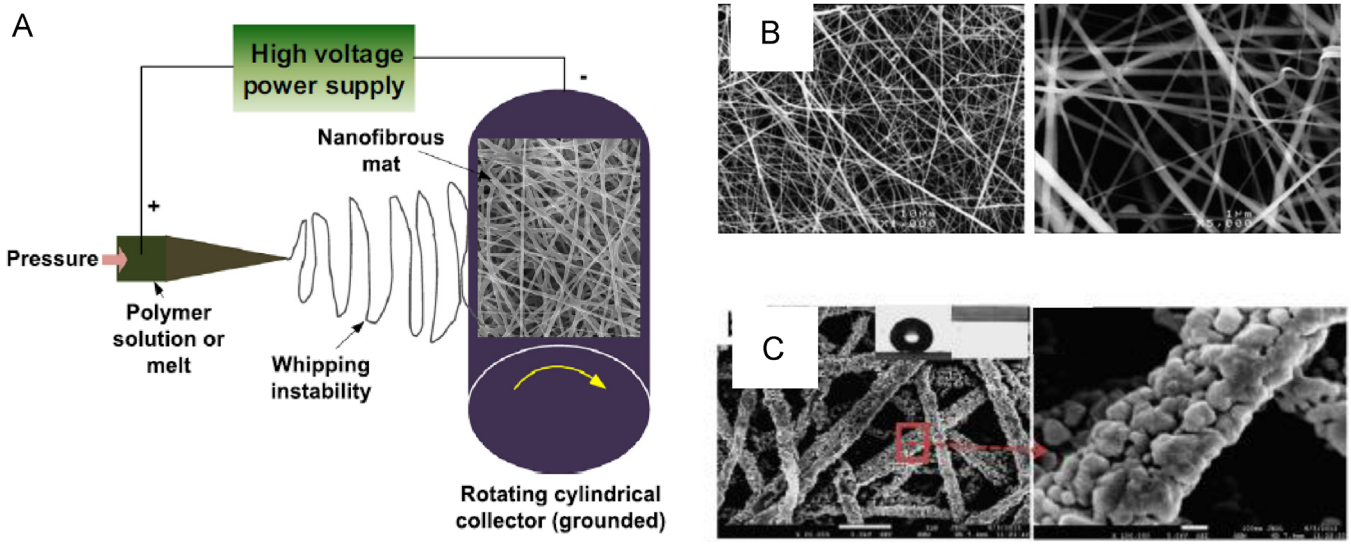


Fig. 2.6. (A) The mechanism and typical set-up of an electro-spinning process, (B) morphology of an electro-spun PVDF membrane, (C) surface modified electro-spun membranes with multi-level roughness [34,143,146].

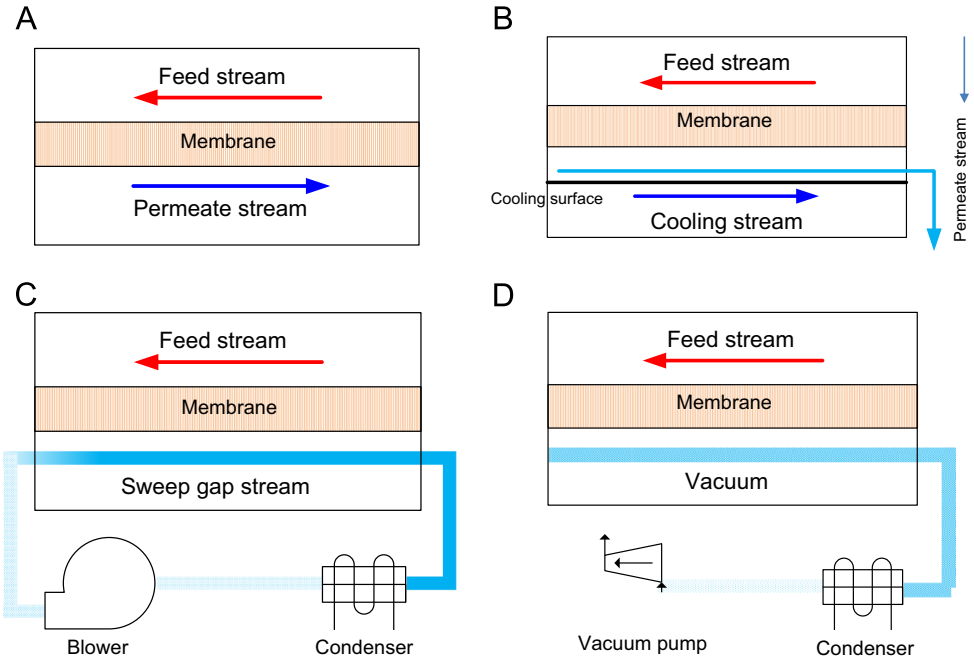


Fig. 3.1. Illustration of a basic MD configurations: (A), DCMD, (B) AGMD, (C) SGMD and (D) VMD.

the aid of heat recovery design and optimal operation conditions, the specific energy consumption of this module for desalination can be as low as 130 kwh/m^3.

3.2.2. *Vacuum multi-effect membrane distillation (VMEMD)*

VMEMD shares a similar concept with the multi-effect membrane distillation (MEMD) except for the vacuum enhancement. Fig. 3.4 illustrates the multi-effect design of a MEVMD configuration. The typical VMEMD consists of a heater, multiple evaporation–condensation stages and an external condenser [49]. A vacuum condition is employed at the air gap region to remove the excess air/vapor. Distillate is hence produced in both condensation stages and inside the condenser. The feed in each stage recovers the condensation heat and a multiple-effect characteristic.

Memsys and its partners invented a series of plate-frame MEVMD and built an automated manufacturing line for membrane modules. The dimension of a typical Memsys module is 330 mm × 700 mm × 480 mm [50]. It uses a PTFE membrane with an average pore size of 0.2 μm as the MD membrane and a 40 μm dense PP film as the condensation layer. The Memsys MEVMD modules have been studied for groundwater purification, moisture removal, brine concentration, solar-driven desalination and others [51,174,175]. Memsys claimed a specific energy consumption value of 175–350 kWh/m^3 [10].

3.2.3. *Hollow fiber multi-effect membrane distillation*

Qin et al. from Chembrane Research & Engineering, Inc. patented a multi-effect AGMD hollow fiber module with internal heat recovery [176]. Unlike the PGMD design, the feed solution is pre-heated to 90 °C before entering the MD module. At the exit of the MD module, the concentrated feed solution at a reduced temperature is further cooled down by an external cooler. This cooled feed solution is fed back into the MD module and serves as the coolant to condensate vapor in the permeate side. As a multi-stage design, the effluent stream can serve as the feed solution for the next membrane module to enhance heat recovery and efficiency. The water flux of their modules for sweater desalination was around 3–10 LMH. With optimal operation conditions, the performance ratio

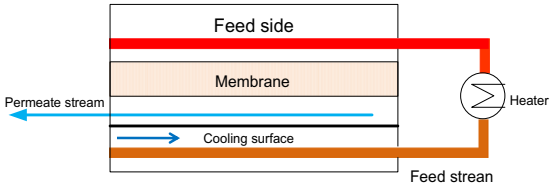


Fig. 3.2. Illustration of an AGMD configuration with internal heat recovery.

(PR) of this module can reach 11.5, which translates into a specific energy consumption around 55 kWh/m^3 [177]

3.2.4. *Material gap membrane distillation (MGMD)*

Due to the presence of a layer of stagnant air between the membrane and the condensation surface, AGMD normally shows a lower permeation flux as compared with other MD configurations. To abate this disadvantage, Francis et al. developed a new MD module design called material gap membrane distillation (MGMD) [178]. The air gap in the module was filled with different materials like sponge (polyurethane) and PP mesh. As a result, an increase of 200–800% in water vapor flux was observed during the MGMD.

4. Applications and Hybrid systems of MD processes

4.1. *Applications of MD processes*

4.1.1. *Seawater/brackish water desalination*

The water availability for human consumption is continuously decreasing due to rapid industrialization and population growth. MD was originally designed for seawater desalination, but the studies of MD for brackish water desalination have gradually attracted interests from both academia and industry [6,20,179].

A small pilot plant was set up by Song et al. for DCMD based desalination and operated successfully on a daily basis for three months [3]. The hot brine tested was either city water containing salt at the level of 3.5, 6 or 10%, or seawater. The plant was operated successfully with a very limited flux reduction at salt

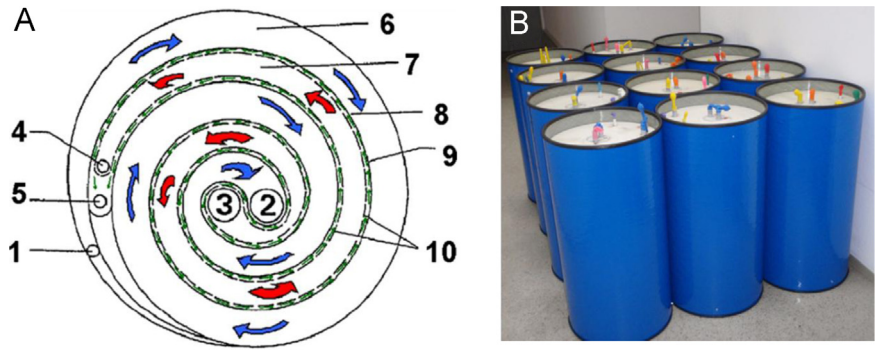


Fig. 3.3. A: Schematic of the spiral wound module concept: (1) condenser inlet, (2) condenser outlet, (3) evaporator inlet, (4) evaporator outlet, (5) distillate outlet, (6) condenser channel, (7) evaporator channel, (8) condenser foil, (9) distillate channel and (10) hydrophobic membrane. B: Ready to use spiral wound desalination modules with a membrane area of 14 m^2 [96].

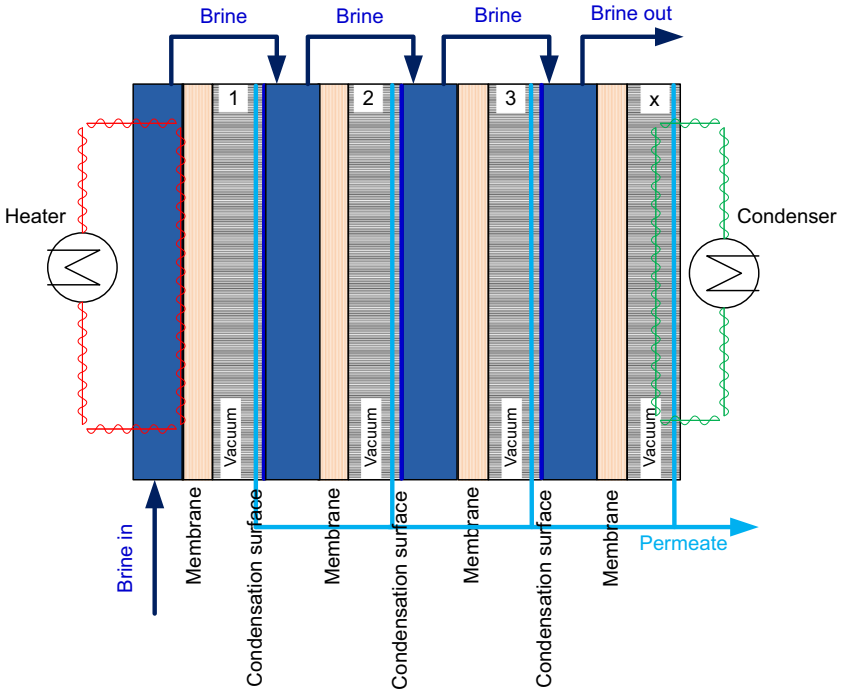


Fig. 3.4. Illustration of a MEVMD configuration [modified from [49]].

concentrations up to 19.5% from sea water. Pilot desalination plants have been built with the commercialized MD systems [51,170,180]. Guillén-Burrieza reported an optimal operation using a multi-stage AGMD module which showed a specific energy consumption of 294 Kwh/m^3 [180]. The AGMD Scarab AB system with heat recovery design has been tested in different desalination projects worldwide [173,181]. Bench and pilot Memstill® modules with heat recovery were tested in Singapore and Netherland before being commercialized [147]. Demonstration desalination plants with VMEMD Memsys systems were also tested in Singapore and China [182].

4.1.2. *Removal of small molecule contaminants*

Membrane technologies such as NF, RO and electro-dialysis (ED) have been widely used for wastewater treatment. In recent years, concerns on poor removal efficiency of small molecule contaminants and heavy metal ions are growing [183,184]. Hence, MD has received attention because it may provide better rejections towards these contaminants.

Boron-containing compounds are commonly found in wastewater or saline water in Asia, North America and Australia [185]. However, rejections of toxic boron-containing compounds by a RO or ED process are only 30–50% depending on the pH value of feed solutions [186]. MD has demonstrated its superior performance in the removal of boron contaminants with a rejection $>99.8\%$ [185,187]. Almost complete rejections were also reported on other heavy metals such as arsenic, chromium or gold [188,189].

The treatment of colored wastewater is of big importance [190]. Usually, a combined coagulation/flocculation, adsorption and UF or NF are applied. Criscuoli et al. reported a complete dye removal using VMD [187]. Khayet et al. also investigated the use of MD to treat wastewater containing radioactive substances [191]. By using both laboratory and pilot systems, MD was found to be an alternative for liquid nuclear waste treatment.

Oil-water separation has received worldwide attention recently due to large amounts of discharged oily wastewater from industries. Free oily wastewater and dispersed oily wastewater have commonly been treated by gravity and skimming, dissolved air flotation, de-emulsification, coagulation and flocculation techniques. However,

there is lack of an effective method to treat stable emulsified oily wastewater [192,193]. Since no hydraulic pressure is applied, MD shows less fouling tendency and has potential for oily wastewater treatment. Using a plasma-modified PVDF membrane, a stable MD performance was reported over 24 h with oily feed water [85]. pH and solution hydrodynamics were found as important parameters affecting oil fouling behavior. The Memsys system was also evaluated for oil-water separation [194]. By modifying the Memsys PTFE membrane with fluoride to improve its oil resistance, the Memsys system showed a stable 6-h operation with feed seawater containing 0.1 wt% oil.

Produced water is a byproduct wastewater stream normally associated with the hydraulic fracturing process in the oil and gas industry. Produced water contains dispersed oils, suspended particles, chemicals as well as salty water. They must be treated prior to being discharged. Due to the high salinity, it's difficult to treat the produced water with RO. MD has been proven as a promising technology for desalting highly saline water with or without pretreatments [11,12,195]. As an example, produced water from the steam assisted gravity drainage (SAGD) process is typically at 80–130 °C and 2–3 atm. Singh and Sirkar utilized this residue heat to process the produced water by DCMD comprising PTFE membranes [195]. The highest water vapor flux achieved was 195 LMH. Zhang et al. designed an integrated forward osmosis and MD process to recover water and acetic acid from produced water [196]. In 2013, GE and Memsys have successfully tested its MD system to concentrate produced water from the hydraulic fracturing process [156]. The field test results showed no noticeable decline in performance and stable performance with brine concentrations near saturation.

Besides the contaminants mentioned above, MD operations were carried to remove organic contaminants such as ammonia, aromatic compounds, trichloroethane and halogenated VOCs [197–201].

4.1.3. Recovery of valuable components

Due to the unique transport mechanism, MD processes have been widely explored for the recovery of valuable components. Based on the volatility and vapor pressure, these components can be concentrated either in the feed stream or permeate stream. Examples include mineral acids, fruit juices, sugar, alcohols and others [158,202–206]. Specifically, concentration of sulfuric acid from 16% until 40% was reported with a separation coefficient of above 98% [207]. Studies were conducted to concentrate the fruit juices [206,208] as well as sugar, herbal extracts and small organic molecules by MD [209–212].

Substances that are more volatile than water, such as volatile acids and alcohols, are enriched in the permeate stream of MD processes [153,157,164,196,207]. One of most studied applications is the separation of volatile acid from its aqueous solutions [213]. Waste streams containing volatile acids such as hydrochloric acid (HCl) are commonly generated from rare earth mining and metallurgical industry. The MD process has demonstrated its capability in volatile acid recycles [214–216]. MD was also widely explored for the separation of alcohols and volatile organic compounds [152,217–220]. The permeate flux was found to be strongly affected by the feed temperature and ethanol/organic concentration in the feed [220]. Hence, only dilute aqueous solutions were tested by AGMD and VMD configurations.

4.2. MD based Hybrid separation processes

MD has been recognized as one of the most preferred membrane processes for hybrid separation technologies [221]. On one hand, with a minimum capital cost, MD can be readily integrated into the existing plant as it is not a pressure-driven process [222–224]. On the other hand, the separation performance of the MD process is less affected by the high salt concentration. As a result, it can significantly enhance the total water recovery (TWR) [225,226]. This section reviews various MD based hybrid processes [221,225,227,228].

4.2.1. Integration with the existing desalination process

Incorporation of MD into the desalination process can dramatically reduce brine discharge and therefore enhance water recovery [229]. Several works have reported positive results by integrating MD with NF or RO desalination [13,127,230–233]. De Andres et al. integrated MD with an existing multi-effect distillation (MED) unit [227]. The overall production of fresh water and energy efficiency has increased by 7.5% and 10%, respectively. The scaling of inorganic salt crystals is the main concern when MD is integrated into current desalination processes. Inorganic salts in the brine such as Ca^{2+} will cause severe scaling in the MD process. Qu et al. integrated an accelerated precipitation softening process with DCMD with a high recovery for the desalination of RO brine [234].

Freeze desalination (FD) refers to the process in which fresh water is extracted by harvesting and melting the ice crystal from saline water [235]. It is a promising desalination technology that could utilize waste cold energy such as liquefied natural gas (LNG) cold energy [225,236]. However, the low water recovery has severely limited the application of FD technology. In order to enhance the water recovery and the utilization efficiency of the cold energy, Wang and Chung proposed the FD-MD process for seawater desalination [225]. The brine from the FD process was further concentrated in the MD process; clean water was obtained from both processes. A high total water recovery of 71.5% was achieved.

4.2.2. Forward osmosis-membrane distillation (FO-MD)

Besides the combination of membrane process and traditional separation technologies, researches have been carried out to integrate the MD process with other membrane processes. For instance, several research groups have worked on the hybrid forward osmosis-MD (FO-MD) process. FO refers to the spontaneous transport of water across a semi-permeable membrane driven by an osmotic pressure gradient [237,238]. Credit to the anti-fouling properties of FO processes, the hybrid FO-MD process can be sustainable under robust feed conditions [239]. A typical FO-MD process was shown in Fig. 4.1 [223]. The FO process draws clean water from the feed solution to the draw solution side, while the MD process is utilized to re-concentrate the diluted draw solution.

The concept of combining FO and MD was firstly proposed in a U.S. patent application [240]. Yen et al. pioneered the real demonstration [241]. Later, Wang et al. explored the process for the concentration of proteins. It could preserve the proteins or pharmaceutical compounds while maintaining high rejections. Other applications that have been explored included heavy metal removal, wastewater treatment, oil removal, dye removal and others [196,239,242–244]. One of the major challenges faced by the combined FO-MD process is the invention of the suitable draw solution. The ideal draw solution should have a high FO flux, low reverse salt leakage and should not cause severe concentration polarization in the MD process. Draw solutes such as inorganic salt and sugars, were used in early stages [239,242]. However, similar to the standalone FO process, the current FO-MD hybrid process is affected by the high reverse draw solute flux (i.e., draw solute leakage). Recently, novel draw solutes were proposed and synthesized based on different chemical structures [241,245,246]. Ge at al. synthesized the draw solutes based on polyelectrolyte which had good solubility in water, high water flux and low salt leakage.

When used in a standalone FO process, polyelectrolytes showed a lower flux due to its high viscosity [245]. In the FO-MD process, the flux was significantly enhanced as the polyelectrolytes viscosity decreased with increasing temperatures.

4.2.3. Membrane distillation-crystallizer (MD-C)

As MD is able to produce highly concentrated brine, with the aid of crystallizers (C), the hybrid (MD-C) process could be a possible solution to achieve a higher recovery for seawater desalination and wastewater treatment [247]. In any MD-C, MD is used for water recovery and to concentrate the feed solution until a desired concentration so that salt crystals can be easily precipitated out by the external crystallizer. As early as 1989, Wu and Drioli have reported the study of MDC for concentrated salt solutions, where crystallization was observed outside the MD membrane module [248]. Similar ideas have been applied to separate inorganic salts, wastewater, protein solution and so on [13,226,249]. Fig. 4.2 shows a typical flow diagram for a continuous MD-C reported by Edwie et al. [249].

4.2.4. Membrane distillation-bioreactor (MDBR)

Membrane bioreactors (MBR) employ UF or micro-filtration (MF) membranes to separate suspended solids from the treated effluent. The incorporation of membranes into the bioreactors have greatly reduce the footprint and is widely used nowadays. However, the UF/MF process is not efficient enough in retaining biodegraded organic solutes. As a result, the organic content increases in the permeate stream [250]. Phattaranawik et al. submerged a MD module into a bioreactor for wastewater treatment [251]. Comparing with the traditional MBR, MDBR has a better permeate quality but a lower flux in the range of 2–5 LMH at atmospheric pressure.

Works have been carried out to integrate MD with a photo-catalysis process for the degradation of organic pollutants in aqueous solutions [252]. Unlike MF or UF, no severe decline was observed in the MD permeation flux. In addition, an almost complete rejection of the model dye contaminant, total dissolved solid and inorganic ions was achieved.

4.2.5. Renewable/waste energy driven membrane distillation

Comparing with RO processes, the energy consumption of MD processes is high. Hence, there are many interests in utilizing renewable energy and industrial waste heat to drive MD processes. Since MD does not operate at extremely high temperature, the utilization efficiency of solar energy or waste heat is very high [96,154,180, 253–256]. Other renewable heat sources such as geothermal energy, residue heat from produced water and hot cooling tower water were also explored to drive MD processes [168,195,254].

In order to ensure high energy efficiency and lower cost in solar-driven MD processes, solar collectors are often employed as the main solar energy collection unit [255,256]. The more expensive photo-voltaic (PV) panel is only used when electricity needs to be supplied for the circulation pumps. For example, a solar-MD system with two solar loops, namely, solar collectors and PV panels were developed with four MD modules [257]. Due to the natural fluctuations of solar radiation, the flux obtained for each solar collector area varied between 2–11 liter/day/m^2. It is also mentioned that the membrane wetting and the scaling are the most serious problems. Fig. 4.3 shows the flow diagram of two-loop solar-MD system [257].

In another work, Cipollina et al. developed a laboratory scale MD unit with a planar geometry for solar seawater desalination [258]. Conceptually simple, the original membrane module consists of multi-stage arrangement and internal heat recovery. It is able to integrate with a polymeric heat exchanger for brine heating by solar energy. Besides AGMD based MD units with internal heat recovery, DCMD or VMD processes with external heat exchangers were also investigated for the utilization of solar energy [259–260].

5. Conclusions and future directions

With the rapid changes in energy price and clean water shortage, the end use of MD has been expanded from initially seawater desalination to many other applications including wastewater treatment and recovery of valuable compounds. To meet the demands from new applications, breakthroughs in material development and membrane fabrication have been made for MD membranes. Materials from traditional hydrophobic materials such as PVDF, PTFE and polyolefins have been extended to new materials including inorganic materials, carbon nano-tubes, and modified hydrophophilic materials. Fabrication methods for MD membranes have also been advanced to comprise dual-layer hollow fiber spinning, multi-bore fiber spinning, and electro-spinning.

Currently, the microporous PTFE membrane dominates the applications in the commercial and pilot MD modules because of its high hydrophobicity and excellent resistance towards harsh operation conditions. However, its high cost and difficulties in module sealing are the major drawbacks. MD membranes made from low cost materials with excellent thermal stability and high hydrophobicity

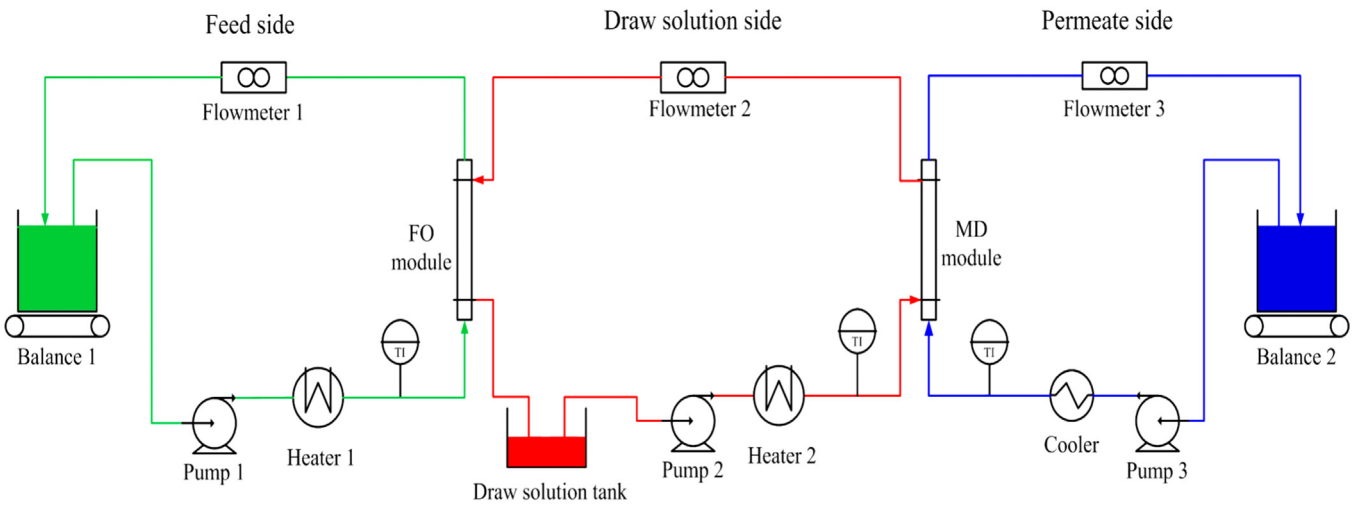


Fig. 4.1. The schematic design of a FO-MD process [223].

are urgently needed. In addition to continuously use aforementioned methods to fabricate MD membranes, focuses should also be given to revolutionary fabrication technologies such as nonwoven supported PVDF hollow fiber spinning process, combined thermal-nonsolvent induced phase separation (TNIPS) process, hydrophobic ceramic membrane fabrication, and others. Considering the increasing MD application in contaminated water purification, attentions might be drawn on the fabrication of membranes with better resistance towards fouling/scaling of organic matters and other contaminants.

High energy consumption is the most challenge to fully commercialize the MD technology. One should consider using the design of the existing multi-effect distillation or others to lower the energy consumption for MD systems. In addition, more research should focus on the effective utilization of low-grade energy sources or renewable energy for MD operations. Since MD can operate at higher salt concentrations, one should integrate MD with other separation technologies such as RO, FO, crystallization and bioreactor in order to maximize the overall performance.

As a non-pressure driven process, MD applications have great potentials in those tough-to-treat wastewater streams where traditional membrane processes have problems, for instance, high salinity produced water from oil & gas fields. More R & D and

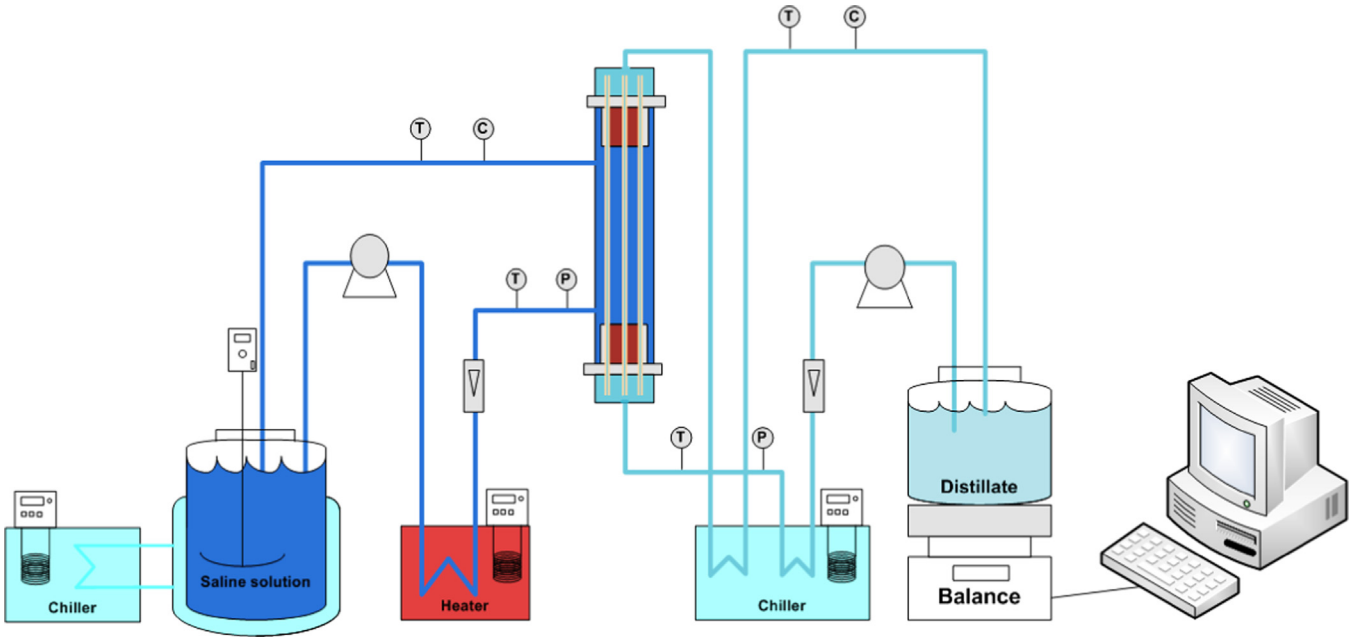


Fig. 4.2. Process flow diagram of a membrane distillation crystallizer (MD-C) [249].

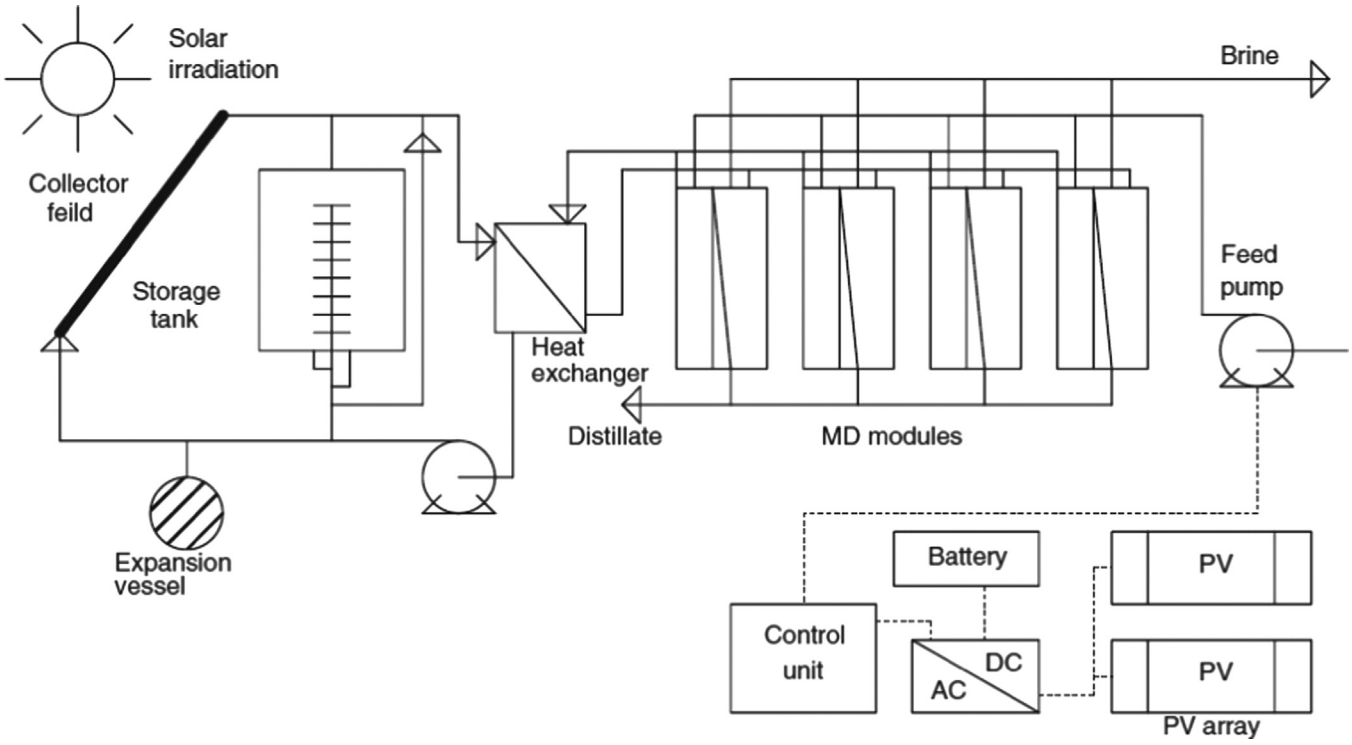


Fig. 4.3. Flow diagram of a compact solar-MD system with solar collector and PV panel [257].

innovations are still needed to find its suitable applications and to minimize the high energy consumption for MD.

Acknowledgements

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